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(54) FLAME-RETARDANT RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a flame-retardant resin composition having high flame retardancy (UL-94, 1/32 inch, V-O), exhibiting good heat-resistance to cause little scorch in molding and giving a molded article with little bleed-out.

SOLUTION: This resin composition is composed of (A) 100 pts.wt. of a polyolefin resin, (B) 1-30 pts.wt. of a mixture of (b1) bis(2,3-dibromopropyl) ether of tetrabromobisphenol A and (b2) bis(2,3-dibromopropyl) ether of tetrabromobisphenol S or (b3) tris(2,3-dibromopropyl) isocyanurate, (C) 0.5-20 pts.wt. of antimony oxide and (D) 0.05-2 pts.wt. of a hydrotalcite. The mixing weight ratio of (b1):(b2) or (b1):(b3) is 1:9 to 9:1.

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CLAIMS

[Claim(s)]

[Claim 1] (A) The polyolefine system resin 100 weight section and the screw (2, 3-dibromopropyl) ether of (B) (b1) tetrabromobisphenol A, The screw (2, 3-dibromopropyl) ether of the tetrabromo bisphenol S or (b3) the mixture 1 with tris (2, 3-dibromopropyl) isocyanurate - 30 weight sections, the (C) antimony oxide 0.5 - 20 weight sections (b2) and -- from the (D) hydrotalcites 0.05 - 2 weight sections -- becoming -- the mixing ratio of a component (b1) and a component (b2) -- or (b1) Flame-retardant-resin constituent whose mixing ratios of a component and a component (b3) are 1:9-9:1 in a weight ratio.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a flame-retardant-resin constituent useful to fabrication of mold goods (a connector, substrate electrode holder, etc.) which consist of present fire retardancy polyolefine material, such as a charge of a sheathing material, internal parts (housing etc.), etc. which need fire retardancy, such as home electronics, OA product, and an automobile field, in detail about a flame-retardant-resin constituent.

[0002]

[Description of the Prior Art] Although the polyolefine is used in the field extensive as a molding material taking advantage of the outstanding property, since a polyolefine is an inflammability, fire retardancy is required in many cases by using it as an industrial material. Although the method of adding various halogenated compounds, such as deca BUROMO diphenyloxide, is conventionally proposed as the flameproofing method of a polyolefine, there are few resin constituents in which it is satisfied [with] of the thermal resistance at the time of a fabricating operation and the bleeding nature in a final product, and a fire-resistant high effect is shown.

[0003] As a method for giving fire retardancy to a polyolefine, the screw (2, 3-dibromopropyl) ether of tetrabromobisphenol A and the screw (2, 3-dibromopropyl) ether of the tetrabromo bisphenol S are used together as a flame retarder. The method (JP,57-73032,A) of improving the bleeding nature in mold goods, the method (JP,9-87437,A) of blending the aluminum salt of a fatty acid with the mixture of the screw (2, 3-dibromopropyl) ether of tetrabromobisphenol A and the screw (2, 3-dibromopropyl) ether of the tetrabromo bisphenol S, etc. are proposed. However, it cannot say that these flame-retardant-resin constituents have enough thermal resistance, but there is a trouble of being easy to produce burning at the time of a fabricating operation for this reason.

[0004]

[Problem(s) to be Solved by the Invention] this invention can cancel the trouble of the aforementioned conventional technology, and can give advanced fire retardancy (UL-94, 1/32 inch, V-0), and since thermal resistance is good, there is little burning at the time of processing, and it aims at a bleed out providing mold goods with a few flame-retardant-resin constituent.

[0005]

[Means for Solving the Problem] Then, wholeheartedly, as a result of research, this invention persons found out that the resin constituent not only fire retardancy but whose thermal resistance improved by carrying out the amount combination of specification of the hydrotalcites into the screw (2, 3-dibromopropyl) ether of tetrabromobisphenol A, the screw (2, 3-dibromopropyl) ether of the tetrabromo bisphenol S, or mixture with tris (2, 3-dibromopropyl) isocyanurate was obtained to the polyolefine system resin, and completed this invention to it. this invention Namely, the (A) polyolefine system resin 100 weight section and the screw (2, 3-dibromopropyl) ether of (B) (b1) tetrabromobisphenol A, It consists of the mixture 1 with the screw (2, 3-dibromopropyl) ether of the tetrabromo bisphenol S, or (b3) tris (2, 3-dibromopropyl) isocyanurate - the 30 weight sections, and the (C) hydrotalcites 0.05 - 2 weight sections. (b2) (b1) the mixing ratio of a component and a component (b2) -- or (b1) The flame-retardant-resin constituent whose mixing ratios of a component and a component (b3) are 1:9-9:1 in a weight ratio is offered.

[0006]

[Embodiments of the Invention] In the resin constituent of this invention, as a polyolefine system resin of the (A) component, a polypropylene regin, a polyethylene system resin, a polybutene system resin, the poly pentene system resin, etc. are mentioned, for example, the copolymer which makes a propylene homopolymer (polypropylene) and a propylene a principal component as a polypropylene regin is mentioned.

- [0007] As the above-mentioned copolymer, a propylene / alpha olefin copolymer is mentioned and ethylene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-butene, 1-pentene, etc. are mentioned as an alpha olefin, for example.
- [0008] As the above-mentioned polyethylene system resin, an ethylene homopolymer (polyethylene) and the copolymer which makes ethylene a principal component are mentioned.
- [0009] As the above-mentioned copolymer, ethylene / alpha olefin copolymer is mentioned and 1-hexene, 4-methyl-1-pentene, 1-octene, 1-butene, 1-pentene, etc. are mentioned as an alpha olefin, for example.
- [0010] As polyolefine system resins other than the above, ethylene / vinyl acetate copolymer, ethylene / ethyl acrylate copolymer, etc. are mentioned, for example.
- [0011] As a polyolefine system resin used by this invention, you may be the mixture of the above-mentioned polyolefine system resin. Especially in this invention, polypropylene is desirable, and especially the polypropylene of 1-70 has desirable flow REITO measured on conditions (230 degrees C and 2.16kg) from the point of acquiring good injection-molding nature and good physical properties.
- [0012] (B) A component is the mixture of the screw (2, 3-dibromopropyl) ether of tetrabromobisphenol A (b1), and the screw (2, 3-dibromopropyl) ether of the tetrabromo bisphenol S, or (b1) the mixture of the screw (2, 3-dibromopropyl) ether of tetrabromobisphenol A, and tris (b3) (2, 3-dibromopropyl) isocyanurate. (b1) the mixing ratio of a component and a component (b2) -- or (b1) Although the mixing ratios of a component and a component (b3) are 1:9-9:1 in a weight ratio, 5:5-7:3 are desirable. (b1) If the bleeding nature in mold goods will get worse if the rate of a component exceeds 9, and the rate of a component (b2) exceeds 9, since fabricating-operation nature (workability) will get worse, the cost of mold goods will become high. In addition, when the melting point of a component (b2) of the screw (2, 3-dibromopropyl) ether of the tetrabromo bisphenol S of a component (b2) increases more than the polyolefine system resin of the (A) component in a degree very much for a low reason, a slip of the screw of a making machine is large and the bird clapper of fabricating-operation nature getting worse is the cause. Moreover, if the rate of a component (b3) exceeds 9, since bleeding nature gets worse, it is not desirable.
- [0013] (B) Although the loadings of a component are 1 - 30 weight section to the polyolefine system resin 100 weight section of the (A) component, its 3 - 15 weight section is desirable. It becomes [if there are few these loadings than 1 weight section, sufficient fire-resistant performance will not be obtained, but / if / than 30 weight sections / more, while physical properties will fall / corning in the shape of a pellet] impossible and is un-economical.
- [0014] (C) The antimony oxide of a component is added as a fire-resistant assistant of a flame retarder [(B) Component], and an antimony trioxide (Sb 2O₃), antimony pentoxide (Sb 2O₅), etc. are mentioned. Although the addition of an antimony oxide is 0.5 - 20 weight section to the polyolefine system resin 100 weight section of the (A) component, its 1 - 10 weight section is desirable. If there are few these additions than the 0.5 weight section, sufficient synergistic effect with a flame retarder is not acquired, especially even if [than 20 weight sections] more, a fire-resistant effect does not improve, either, and physical properties fall and are un-economical.
- [0015] (D) As hydrotalcites of a component, there are a natural product and synthetic compounds, what does not contain hydrate-salt machine nature carbonates, such as magnesium, calcium, zinc, aluminum, and a bismuth, or the water of crystallization of those mentions, and it is ****. As a natural product, it is Mg₆ aluminum₂. What has the structure of (OH)₁₆CO₃ and 4H₂O is mentioned. As synthetic compounds, it is Mg_{0.7} aluminum_{0.3}. (OH) 20.15.0.54 (CO₃) H₂O, Mg_{4.5} aluminum₂ (OH)₁₃CO₃ and 3.5H₂O, and Mg_{4.2} aluminum₂ (OH)_{12.4}(CO₃) 0.15 and Zn₆aluminum₂ (OH)₁₆CO₃ and 4H₂O, calcium₆ aluminum₂ (OH)₁₆CO₃ and 4H₂O, and Mg₁₄Bi₂ (OH)_{29.6.4.2}H₂O etc. is mentioned.
- [0016] The addition of the (D) component in the constituent of this invention is 0.05 - 2 weight section to the polyolefine system resin 100 weight section of the (A) component. Fire retardancy falls and is un-economical if [than 2 weight sections] more [sufficient thermal resistance will not be discovered if there are few these additions than the 0.05 weight section, and].
- [0017] The bulking agent usually blended with a resin constituent if needed in the range which does not spoil the purpose of this invention other than the above-mentioned component, lubricant, an antioxidant, an antistatic agent, an ultraviolet ray absorbent, a pigment, etc. can be suitably blended with the flame-retardant-resin constituent of this invention.
- [0018] The resin constituent of this invention can be manufactured by carrying out melting kneading of each above-mentioned component by arbitrary methods. If the example is given, there is a method of being independent, or combining and using the continuation kneading machine of the high-speed agitator represented by the Henschel mixer, a monopodium, or two shafts, a roll mixer, etc. Thus, although there is especially no limit in the method of fabricating the obtained resin constituent and there are methods, such as injection molding, extrusion molding, and blow molding,

in it, especially injection molding is suitable.

[0019]

[Example] Next, this invention is not limited by these examples although an example explains this invention to a detail further. In addition, the matter used for a following example and the following example of comparison is as follows.

1) Polypropylene Idemitsu polypropylene J2003GP (MI=21g /, 10 minutes)

In addition, MI value of polypropylene was measured on conditions (230 degrees C and 2.16kg) using the testing machine (made in Oriental Energy Machine Factory, melt indexer S-001).

2) The screw (2, 3-dibromopropyl) ether Dai-Ichi Kogyo Seiyaku Co., Ltd. make of tetrabromobisphenol A, PIROGADO Product made from the formation of screw (2, 3-dibromopropyl) ether ***** of the SR7203 tetrabromo bisphenol S, NONNEN PR-24 tris (2, 3-dibromopropyl) isocyanurate Asahi Glass Co., Ltd. make, AFR10025 antimony-trioxide mean particle diameter The product made from 1-micrometer6 Hydrotalcite Consonance Chemistry, DHT-4A. [0020] Melting kneading of the combination component shown in examples 1-8 and the example 1 of comparison - the 5 1st table was carried out at 120-240 degrees C using the 2 shaft kneading machine (the tradename PCM 45 made from IKEGAI Steel), the constituent was produced, and it pelletized using the strand cut. In this way, injection molding of the obtained constituent pellet is carried out using the injection molding machine (tradename FE-120, PS-40) by NISSEI PLASTIC INDUSTRIAL CO., LTD. at 190-210 degrees C of cylinder temperatures, and 50 degrees C of die temperatures, a test piece is produced, and it is the following evaluation method (1) about the property. And (2) It evaluated. Moreover, the following examination (3) It carried out. A result is shown in the 1st table.

[0021] (1) Fire-resistant evaluation (UL-94)

testing-machine: -- the product made from Atlas, and the HVUL plastics UL combustion test chamber examining method -- according to UL-94, the vertical firing examination was performed about the thickness of 1/32 inch of :test piece

(2) Wipe off with an acetone the flame retarder which has oozed out on the front face of a forming plate, and carry out weighing capacity of the forming plate, after using the bleed-out nature injection-molding plate (80x80x3.2mm) on the front face of mold goods as a test piece, carrying out weighing capacity of this, and leaving it in 100-degree C oven for 120 hours. From the weight change before and behind an examination, the rate of bleeding (%) was computed by the following formula.

Rate of bleeding = (weight change before and behind an examination) /(initial mass of test piece) x100 (%)

(3) Thermal resistance (stay burning examination)

injection-molding-machine: -- the NISSEI PLASTIC INDUSTRIAL CO., LTD. make and the PS-40 examining method -- within the cylinder of :injection molding machine, it was made to pile up for 5 minutes, and injection molding of the constituent was continuously carried out at 200-220 degrees C, and the grade of burning of the front face of mold goods (plate) was visually judged by the following criteria

1: 2: with very much burning -- 3: with much burning -- 4: whose burning is a degree in the middle -- 5: with little burning -- burning comes out very only [0022]

[Table 1]

第 1 表-1

	PP	TBA-DBP	TBS-DBP	B-TAIC	Sb ₂ O ₃	MTM
実施例1	100	8	2	-	4	0.3
実施例2	100	6	4	-	4	0.3
実施例3	100	4	6	-	4	0.3
実施例4	100	2	8	-	4	0.3
実施例5	100	6	4	-	4	0.5
実施例6	100	6	4	-	4	1.0
実施例7	100	6	-	4	4	0.3
実施例8	100	4	-	6	4	0.3
比較例1	100	10	-	-	4	-
比較例2	100	-	10	-	4	-
比較例3	100	-	-	10	4	-
比較例4	100	10	-	-	4	0.3
比較例5	100	6	4	-	4	3.0

TBA-DBP: テトラブロモビスフェノールAのビス(2,3-ジブロモ)エーテル

TBS-DBP: テトラブロモビスフェノールSのビス(2,3-ジブロモ)エーテル

B-TAIC: トリス(2,3-ジブロモプロピル)イソシアヌレート

[0023]

[Table 2]

第 1 表-2

	燃焼性 (UL-94, 1/32")	耐熱性	ブリード率
実施例1	V-0	4	0.25
実施例2	V-0	4	0.23
実施例3	V-0	5	0.21
実施例4	V-0	5	0.21
実施例5	V-0	5	0.23
実施例6	V-0	5	0.22
実施例7	V-0	4	0.25
実施例8	V-0	5	0.24
比較例1	V-0	1	0.39
比較例2	V-0	3	0.25
比較例3	V-0	1	0.29
比較例4	V-0	3	0.37
比較例5	V-2	5	0.22

[0024]

[Effect of the Invention] According to this invention, advanced fire retardancy (UL-94, 1/32 inch, V-0) can be given, and since thermal resistance is good, there is little burning at the time of processing, and it can provide mold goods with a flame-retardant-resin constituent with few bleed outs.

[Translation done.]